

Catalytically Enhanced Hydrogen Storage Systems

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Objectives

- Determination of the chemical nature of the titanium species responsible for the enhanced kinetics of Ti-doped NaAlH₄.
- Determination of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes.
- Development of hydrogen storage materials based on complex aluminum hydrides that meet the FreedomCAR hydrogen storage targets of cost, specific energy, and energy density.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan.

- B. Weight and Volume
- C. Efficiency
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Determination and quantification of effective dopant through electron paramagnetic resonance (EPR) and magnetic susceptibility studies.
- Elucidation of the effects of doping directly on hydrogen by neutron diffraction, inelastic neutron scattering (INS), solid state nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.
- Determination of the dependence of plateau pressure on doping level.
- Synthesis and evaluation of advanced alanates suggested by the insight gained by fundamental studies.

Accomplishments

- Verification that doping NaAlH₄ with Ti dopant precursors generates Ti(III) dopants that persist through dehydrogenation and repeated hydrogen cycling.
- First accurate determination of the location of the hydrogen atoms in NaAlH₄ through a neutron diffraction study of NaAlD₄.
- Observation of the bulk perturbation of the [AlH₄]⁻ anion upon doping through ²H NMR and IR spectroscopy studies.

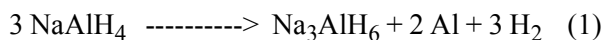
- Measurement of changes in plateau pressure resulting upon variation in level of Ti substitution in NaAlH₄.
- Development of a method for the removal of sodium salt by-products from doped NaAlH₄.

Future Directions

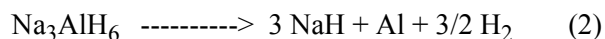
- Continue characterization and quantification of titanium species in doped NaAlH₄ by combination of EPR and magnetic susceptibility and determine whether kinetic enhancement is due to Ti(III) or Ti(IV) species.
- Continue IR, NMR, and INS spectroscopic studies and obtain Raman spectra to elucidate the influence of doping on the dynamics of the [AlH₄]⁻ anion and their relationship to hydrogen cycling kinetics.
- Determine the hydrogen cycling properties of doped NaAlH₄ from which doping by-product(s) have been removed.
- Probe whether the purification method can be extended to hydride containing high (>10 mol %) doping levels and Li- and Mg-based alanates.

Introduction

We have developed methods of doping sodium aluminum hydride, NaAlH₄, with titanium and/or zirconium that give rise to state-of-the-art hydrogen storage materials. During the initial dehydrogenation reaction seen in equation 1, NaAlH₄ rapidly evolves



temperatures upon doping with 2 mole percent Ti(OⁿBu)₄ by our methods. At 100°C, hydrogen flow rates of 0.01 g H₂/s per kg under a constant pressure of 1 atm have been observed. This performance is adequate to meet the demands of a fuel cell operating under practical conditions. We have also found that NaH and Al doped with 2 mole percent Zr absorbs 4.4 weight percent hydrogen within 15 minutes at 120°C under 125 atm of hydrogen pressure. However, despite this progress in enhancing the dehydrogenation and re-hydrogenation processes, it has not yet been demonstrated that ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. Most notably, the rate and equilibrium plateau pressures of the second dehydrogenation reaction, seen in equation 2, are



impractical for hydride that is doped with titanium, and improved variations of this material must be

produced to achieve commercial viability. To guide our development of advanced alanates, we have sought to gain a fundamental understanding of the nature of the dopants and the structural effects they exert on the hydride.

Approach

It was initially speculated that the remarkable enhancement of the hydrogen cycling kinetics in doped NaAlH₄ was due to surface-localized catalytic sites. However, we obtained X-ray crystallographic data that revealed that the doping of the hydride results in bulk lattice distortions. These observations have led us to develop a new model of the doped hydrides in which Na⁺ ions are substituted by M⁴⁺ and/or M³⁺ dopant ions and the generation of the requisite number of Na⁺ vacancies in the hydride lattice to maintain charge neutrality. Spin isolated Ti(III) has been identified in the EPR spectroscopy. This finding is consistent with the presence of the Ti³⁺ cations in the doped hydride as predicted by our “substitution model” of doped NaAlH₄. It also raises the question of whether the enhanced hydrogen cycling kinetics in the doped hydride are the result of substitution of Na⁺ by M³⁺ or M⁴⁺ or both. In a collaborative study with Dr. Sandra Eaton of the University of Denver, we are endeavoring to resolve this ambiguity through further EPR studies in conjunction with quantification of the density of the paramagnetic M³⁺ through magnetic susceptibility experiments.

Although x-ray diffraction and EPR studies showed that the doping of NaAlH_4 results in bulk structural changes, these techniques cannot yield reliable information about the structural environment of the hydrogen atoms. Thus, in order to determine what changes occur in the structural environment of the hydrogen atom upon doping the hydride, neutron diffraction, INS, solid state NMR, and infrared spectroscopic studies are being conducted. We have established collaborations with Dr. Hendrick Brinks and Dr. Bjorn Hauback, Institute for Energy Technology, Kjeller, Norway (neutron diffraction); Terry Udovic, National Institute of Standards and Technology (INS); Dr. Juergen Eckert, Los Alamos National Laboratories (INS); and Prof. Klaus Yvon and Dr. Sandrine Gomes, University of Geneva (IR) for these efforts.

The doping process generates by-products that constitute “dead weight” in the kinetically enhanced hydride. For example, doping with TiCl_3 or TiCl_4 results in the formation of segregated NaCl by-product. Thus, the increased kinetic enhancement at higher doping levels results in a capacity loss due to the weight of **both** the Ti dopant and the by-product. Additionally, the earlier “redox” model of the doped hydride predicts a 3-4 equivalent loss in hydrogen-carrying Al upon doping. By contrast, our “substitution” model of the doped hydride predicts all Al remains available for hydrogen binding. This is an important distinction as only the newer model suggests that removal of “dead weight” doping by-product might lead to materials having both increased hydrogen capacity as well as the highly acceptable kinetics that are achieved at high doping levels. Additionally, the “substitution” model, unlike the redox model, predicts that plateau pressure, a thermodynamic property, should be significantly altered at high doping levels. Thus, we are probing the effect of doping on the equilibrium plateau pressures of the hydride. We are also developing methods of removing the inert, “dead weight” by-products that are generated in the doping process and are measuring the hydrogen cycling capacities and kinetics of these purified materials.

Results

Electron Paramagnetic Spin and Magnetic

Susceptibility Studies: Preliminary electron paramagnetic resonance studies were conducted in

collaboration with Dr. Sandra Eaton, University of Denver, and Dr. Karl Gross and Eric Majoub, Sandia National Laboratory. The EPR spectrum of a sample NaAlH_4 doped with 2 mol % $\text{Ti}(\text{OBu})_4$ is seen in Figure 1. The very sharp, singlet signal that dominates the spectrum can be readily assigned to spin isolated $\text{Ti}(\text{III})$. Very similar spectra were obtained from a variety of samples that were doped with either $\text{Ti}(\text{III})$ or $\text{Ti}(\text{IV})$ precursors. This finding lends strong support for our “substitution” model of doped NaAlH_4 . Continuing collaborative studies with the University of Denver group have shown that the spin isolated $\text{Ti}(\text{III})$ dopants persist through dehydrogenation and in repeated hydrogen cycling of the material. While the EPR studies provide strong support for the substitution of Ti^{3+} , into the bulk hydride lattice, it does not preclude the possibility that EPR silent, diamagnetic Ti^{4+} is also present. In order to explore this possibility, we have begun efforts to quantify the amounts of $\text{Ti}(\text{III})$ present in Ti doped hydride through magnetic susceptibility measurements. At this point we have completed the measurement of χ (magnetic susceptibility) values for a series of standards containing known amounts of $\text{Ti}(\text{III})$ and generated a standard plot of χ vs. moles $\text{Ti}(\text{III})/\text{cc}$. Quantification of the amount of $\text{Ti}(\text{III})$ present in samples of the doped hydride can now be accomplished by comparison of their measured χ

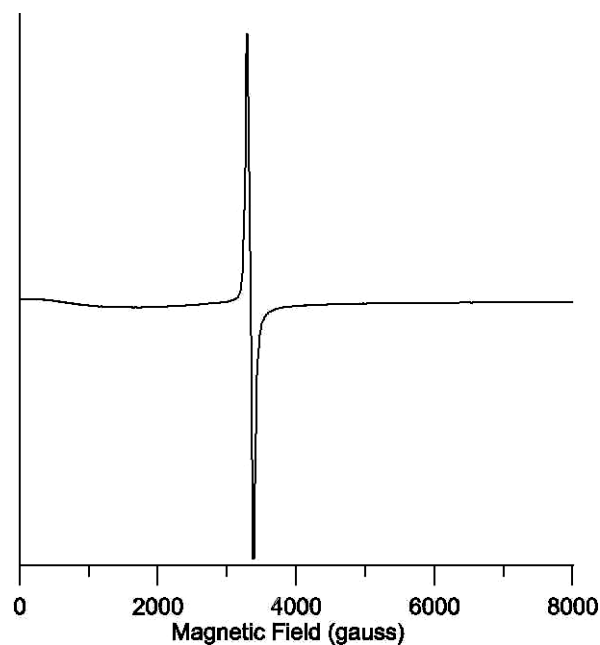


Figure 1. EPR Spectrum NaAlH_4 Doped with 2 mol % $\text{Ti}(\text{OBu})_4$

values to the standard plot. If the level of Ti(III) present is less than the Ti doping level, it can be inferred that the unaccounted titanium is present as diamagnetic, Ti(IV). Determination of the amounts of Ti(III) and Ti(IV) in the doped hydride will allow us to determine if the kinetic enhancement resulting upon doping tracks the level of substitution of Na^+ by Ti^{3+} , Ti^{4+} , or both.

Neutron Diffraction: In order to undertake a neutron structure determination, we had to develop a method for the synthesis of high purity NaAlD_4 . This was accomplished through the reaction of LiAlD_4 with NaF in the presence of an aluminum alkyl catalyst. Neutron diffraction data were collected at the Institute for Energy Technology in Kjeller, Norway, from a sample of NaAlD_4 that was prepared through this method. Final refinement of this data gave the structure of the hydride seen in Figure 2. The deuterium atoms were well located, giving a structure with two unique Al-D distances of 1.627(2) and 1.626(2) Å, and two unique D-Al-D angles of 107.30(1) and 113.90(1).

Infrared Spectroscopy: Preliminary infrared spectroscopic studies have been carried out. No new vibrational modes or changes in absorption frequencies can be detected upon comparison of doped and undoped samples of NaAlH_4 . However, there is a dramatic broadening of the infrared absorptions in the samples of the doped hydride. This finding indicates that while the bonding in the $[\text{AlH}_4]^-$ anion is unperturbed upon doping, the

changes that occur upon bulk Ti^{3+} substitution in the lattice result in a broader allowable range of orientation of the anions in the lattice.

Solid State Nuclear Magnetic Resonance

Spectroscopy: Comparison of the solid state ^2H spectra of doped and undoped samples of NaAlD_4 show a significant broadening of the dipolar doublet upon doping. This finding is in agreement with our interpretation of the IR studies: the changes that occur upon bulk Ti^{3+} substitution in the lattice result in a broader allowable range of orientation of the anions in the lattice.

Effect of Doping Level on Plateau Pressures: The equilibrium hydrogen pressure has been determined for samples of NaAlH_4 that were doped with 1.3 – 2.0 mole % $\text{Ti}(\text{O}i\text{Bu})_4$. The plateau pressure was seen to increase linearly from 3.0(2) to 4.7(2) Mpa over the range of doping levels.

Purification of Doped Materials: A proprietary method has been developed for the removal of the contaminant sodium salts resulting upon Ti doping of NaAlH_4 . X-ray diffraction has shown that the removal of the by-products is >95% complete.

Conclusions

We have, for the first time, accurately determined the location of the hydrogen atoms in NaAlH_4 through a neutron diffraction study of NaAlD_4 . Our EPR, IR, and NMR studies provide additional support for our “substitution” model of doped NaAlH_4 that was initially proposed on the basis of x-ray diffraction data. The ERP studies lend strong support to our hypothesis that Ti doping of the hydride results in the substitution of Ti^{3+} into the bulk hydride lattice that persists through repeated cycles of dehydrogenation/re-hydrogenation. The IR and solid state ^2H NMR studies also provide clear evidence that bulk changes occur in the hydride upon doping. Moreover, the changes in the equilibrium plateau pressures that are predicted by the “substitution” model have been verified. Thus, prospects seem bright for the possibility of tailoring an alanate material with thermodynamic properties well suited for utilization as an onboard hydrogen carrier for PEM fuel cell applications. Furthermore, we have developed a method for the removal of the

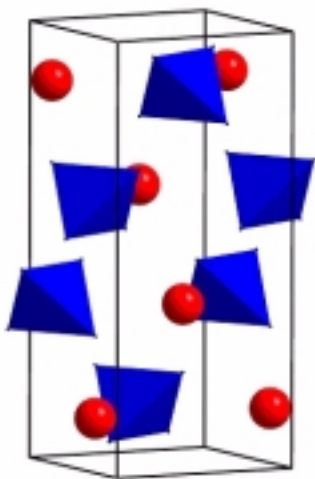


Figure 2. Crystal Structure of NaAlD_4

“dead weight” by-products that result from the doping process. Thus, it may be possible to obtain mixed Na/Ti alanates that contain up to 6 wt % available hydrogen and exhibit superior hydrogen cycling kinetics.

Publications (5/02-6/03)

1. D. Sun, H.T. Takeshita, T. Kiyobayashi, N. Kuriyama, and C.M. Jensen, “X-ray Diffraction Studies of Titanium and Zirconium Doped NaAlH₄: Structural Basis of the Enhanced Hydrogen Storage Properties Resulting Upon Doping”, *J. Alloys Compd.* **2002**, 337, 8.
2. K.J. Gross, C.M. Jensen, and G.J. Thomas, “Catalyzed Alanates for Hydrogen Storage”, *J. Alloys Compd.* **2002** 330-332, 683.
3. G. Sandrock, K. Gross, G. Thomas, C. Jensen, D. Meeker, and S. Takara, “Engineering Considerations in the Use of Catalyzed Sodium Alanates for Hydrogen Storage”, *J. Alloys Compd.* **2002**, 330-332, 696.
4. G.J. Thomas, K.J. Gross, N.Y.C. Yang, C.M. Jensen, “Microstructural Characterization of Catalyzed NaAlH₄”, *J. Alloys Comp.* **2002**, 330-332, 702.
5. B.C. Hauback, H. W. Brinks, C.M. Jensen, K. Murphy, and A.J. Maeland, “Neutron Diffraction “Structure Determination of NaAlD₄” *J. Alloys Comp.* **2003**, 358, 142.
6. S.S. Eaton, K. Gross, E. Majzoub, K. Murphy, and C.M. Jensen, “EPR Studies of Titanium Doped NaAlH₄: Fundamental Insight to a Promising New Hydrogen Storage Material”, *Chem. Commun.*, in press.

7. T. Kiyobayashi, S.S. Srinivasan, D. Sun, and C.M. Jensen, “Kinetic Study and Determination of the Enthalpies of Activation of Titanium and Zirconium Doped NaAlH₄ and Na₃AlH₆” *J. Phys. Chem.*, in press.

Invited Presentations (May 2002 – June 2003)

1. 5/13/02 Symposium on Hydrogen Storage Materials and Hydrogen Generators, 201st meeting of the Electrochemical Society, Philadelphia, PA.
2. 8/13/02 Universal Oil Products Research Center, Des Plaines, Illinois.
3. 9/05/02 International Symposium on Metal Hydrogen Systems, Annecy, France.
4. 9/13/02 California Institute of Technology.
5. 3/18/03 Research Association for the Development of Advanced Metal Hydrides meeting, Osaka, Japan
6. 6/11/03 European Materials Research Society 2003 Meeting, Symposium on Nanoscale Materials for Energy, Strasbourg, France.

FY 03 Patents

1. Craig M. Jensen and Ragaiy. A. Zidan, “Hydrogen Storage Materials and Method of Making by Dry Homogenation”, **2002**, US patent 6,471,935.